Solution to Exercise 4.2-1 "Diffusion During Cooling"

Illustration

For the diffusion length ***L*** we have the well known equations:

$$L = \sqrt{2\,Dt} \quad or \quad L^2 = 2\,Dt$$
$$D = D_0 \exp\left(-\frac{E}{kT}\right).$$

- ***E*** is the activation energy of the diffusing species an **k** is the Boltzmann constant. Because of $T = T_0 \cdot \exp -(\lambda \cdot t)$ we obtain for L^2

$$L^2 = 2\,D(t)t = 2\,D_0 \int_0^\infty \exp\left(-\frac{E}{kT(t)}\right) dt$$
$$= 2\,D_0 \int_0^\infty \exp\left(-\frac{E}{kT_0 \exp(-\lambda t)}\right) dt$$
$$= 2\,D_0 \int_0^\infty \exp\left(-\frac{E}{kT_0} \exp(\lambda t)\right) dt$$

Now we have a purely mathematical exercise which is not too difficult, but not too easy either. In order to solve the integral, we try the substitution

- $$u(t) = \frac{E}{kT_0} \exp(\lambda t), \qquad dt = \frac{du}{\lambda u}$$

- The boundaries must be changed too, we obtain

  t **= 0** changes to $u_0 = E/kT_0$
  t **=** ∞ changes to ***u*** **=** ∞.
  This gives us

$$L^2 = \frac{2\,D_0}{\lambda} \int_{u_0}^\infty \frac{1}{u} \exp(-u)\,du\ .$$

Now you must solve a simple looking integral. There are several ways of doing that

- 1. Find a good math book with lots of integrals and take the solution from there (the "Bronstein", however, won't do)
  2. Do a sensible approximation and solve it yourself in a simple way
  3. Go all the way and solve it completely - if you can.
- Here we go the second route.

We use a Taylor expansion for $1/u$ around u_0 because that's where ***u*** is felt most critically - for large values of ***u*** everything tends to be zero anyway. In full generality we have

$$\frac{1}{u} = \sum_{\nu=0}^{\infty} (-1)^\nu \frac{1}{u_0^{\nu+1}} (u - u_0)^\nu \approx \frac{1}{u_0} - \frac{u - u_0}{u_0^2}.$$

- If we keep it really simple, we could just use the first term, having $1/u \approx 1/u_0$; but we will go one step beyond this and take

$$\frac{1}{u} \approx \frac{1}{u_0} - \frac{u - u_0}{u_0^2}$$

- This gives us

$$L^2 = \frac{2D_0}{\lambda u_0}\int_{u_0}^{\infty} \exp(-u) - \frac{u-u_0}{u_0}\exp(-u)\,du$$

$$= \frac{2D_0}{\lambda u_0}\int_{u_0}^{\infty} 2\exp(-u) - \frac{u}{u_0}\exp(-u)\,du$$

$$= \frac{2D_0}{\lambda u_0}\left[-2\exp(-u) + \frac{u+1}{u_0}\exp(-u)\right]_{u_0}^{\infty}$$

$$= \frac{2D_0}{\lambda u_0}\exp(-u_0)\left[1 - \frac{1}{u_0}\right]$$

$$= \frac{2D_0 kT_0}{\lambda E}\exp\left(-\frac{E}{kT_0}\right)\left[1 - \frac{kT_0}{E}\right]$$

$$\Rightarrow L = \sqrt{\frac{2D_0 kT_0}{\lambda E}\left[1 - \frac{kT_0}{E}\right]}\exp\left(-\frac{E}{2kT_0}\right).$$

- The second term of the Taylor expansion brought in the factor **[1 – kT_0/E]** and since **kT_0 « E** in all normal cases, it is indeed not very important. If we neglect it, we may simply give the desired solution as

$$L = \left(\frac{2D_0 \cdot kT_0}{\lambda \cdot E}\right)^{1/2} \cdot \exp -\frac{E}{2kT_0}$$

Now we can look at some typical cases and see what this formula means. However, first we have to find the right values for λ

- For this we have to take the given values of the initial cooling rate, which we call **λ'**, and see what λ values correspond to these cooling rates.
- The initial cooling rate **λ'** is the derivative of the ***T*(*t*)** function at ***t* = *t*$_0$ = 0**, we thus have

$$\frac{d}{dt}(T_0 \cdot \exp - \lambda \cdot t)\Big|_{t=0} = \lambda' = -\lambda \cdot T_0 \cdot \exp - \lambda \cdot t\Big|_{t=0} = -\lambda \cdot T_0$$

- and obtain

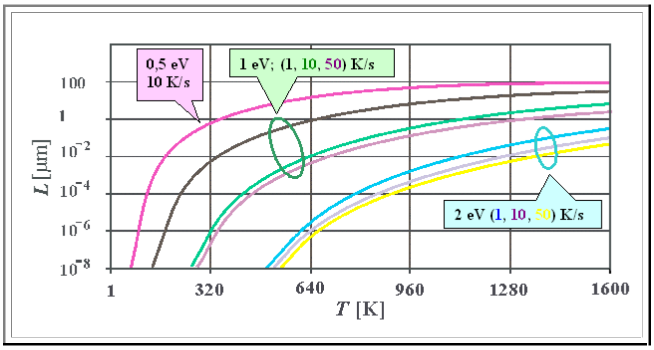
$$\lambda = \frac{\lambda'}{T_0}$$

- The "**–**" sign cancels, because our **λ'** must carry a minus sign, too, if it is to be a cooling and not a heating rate.

Replacing λ by **λ'/T_0** yields the final formula:

$$L = \left(\frac{2D_0 \cdot kT_0^2}{\lambda' \cdot E}\right)^{1/2} \cdot \exp -\frac{E}{2kT_0}$$

- We have to evaluate this formula for cooling rates **λ'** given as (–) **1 ^{o}K/s**, **10 ^{o}K/s**, **50 ^{o}K/s**, **10^4 ^{o}K/s**, and activation energies of ***E* = 1.0 eV, 2.0 eV, 5 eV**. For ***D*$_0$** we take ***D*$_0$ = 10^{-5} cm^{2}s^{-1}**.
- The result (including the **[1 – kT_0/E]** term is shown below



What can we learn from the formula and the curves?

1. The cooling rate is not all that important. Differences in the cooling rate of a factor of **50** produce only an order of magnitude effect or less since ***L*** is only proportional to $(1/\lambda)^{1/2}$.
2. The starting temperature T_0 is slightly more important than the activation energy ***E***; both have the same weight in the exponential, but T_0 appears directly in the pre-exponential while ***E*** enters only as square root.
3. The pre-exponential factor D_0 of the diffusion coefficient is exactly as important as λ' and ***E*** in the pre-exponential factor of the equation for ***L***

What can we do with the numbers? Quite simple:

1. ***L*** gives you the average of the largest distance between some point defect agglomerates, e.g. precipitates, because point defects farther away than ***L*** from some nuclei cannot reach it and must form their own agglomerate.
2. The average number of point defects in an agglomerate divided by L^3 gives a lower limit for the point defect concentration, because at least as many point defects as we find in an agglomerate must have been in the volume L^3.